# A Diels-Alder Approach to the Enantioselective Construction of Fluoromethylated Stereogenic Carbon Centers

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## Supplementary Information

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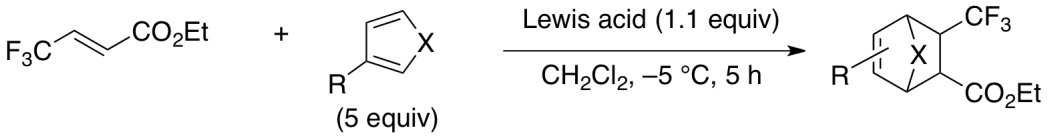
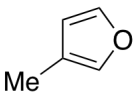
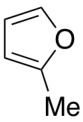
**Diels-Alder reaction of β-trifluoromethylacrylate mediated by achiral Lewis acid**




| Entry | Diene | Lewis acid | Yield (%)[a] | *exo*/*endo*[b] |
|---|---|---|---|---|
| 1[c] |  | $EtAlCl_2$ | 72 | 42/58 |
| 2[c] | | $TiCl_4$ | 19 | 52/48 |
| 3 |  | $EtAlCl_2$ | 95 | 51/49 |
| 4 | | $TiCl_4$ | 22 | 68/32 |
| 5 |  | $EtAlCl_2$ | 98[d] | 35/65 |
| 6 | | $TiCl_4$ | trace | nd |
| 7 |  | $EtAlCl_2$ | 0 | – |
| 8 | | $TiCl_4$ | 0 | – |

[a] Determined by $^{19}F$ NMR with 1,1,1,3,3,3-hexafluoro-2-propanol as an internal standard. [b] Determined by $^{19}F$ NMR. Endo/exo nomenclature is related to the stereochemistry of the carbonyl substituent. [c] 0.5 equivalent of Lewis acid was employed. [d] The reaction yielded a mixture of regioisomers which consists of a 6:4 regioisomeric mixture of exo-adduct and a 9:1 regioisomeric mixture of endo-adduct.

**Hypothetical transition state models**

**Figure S1.**

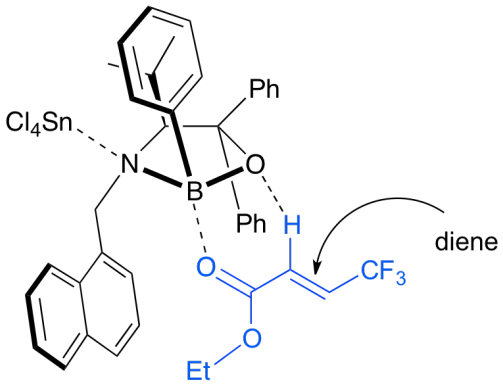



**Figure S2.**

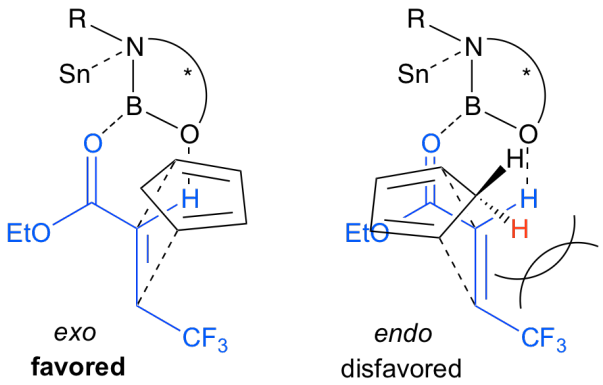
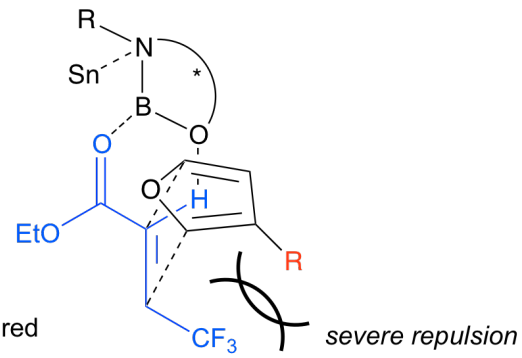
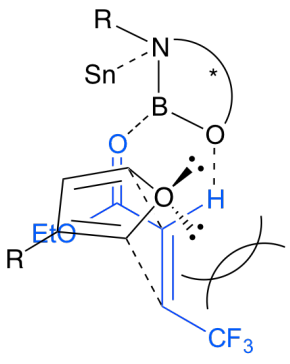



**Figure S3.**



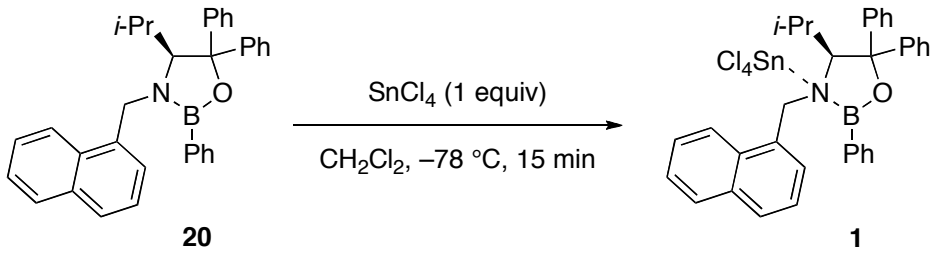

The absolute stereochemical course of the Diels-Alder reactions can be explained by a hypothetical transition state model shown in Figure S1. The model of dienophile complexation to activated oxazaborolidine via the C–H···O hydrogen bonding is analogous to that postulated by Corey et al.[1] As shown in Figure S2, exo-selective cycloaddition of non-substituted cyclopentadiene or furan can be explained by the steric repulsion between a trifluoromethyl group and a hydrogen at C(5) in cyclopentadiene (red hydrogen),[2]

or a lone pair on the oxygen in furan. On the other hand, in the case of the reaction of 3-substituted furan, endo-adducts are preferentially formed owing to the severe steric repulsion between a substituent at C(3) (red R) and a trifluoromethyl group (Figure S3). However, further investigations are needed to clarify the origin of high exo-selectivity in the reaction of 2-substituted furan.

**General**: Thin-layer chromatography analyses were performed using Merck pre-coated silica gel plates with 254 indicator. Flash column chromatography was performed using silica gel 60 (mesh 230-400) supplied by Merck. Infrared spectra were recorded as thin films on sodium chloride plates using a JASCO FTIR-230 spectrometer. $^{1}$H, $^{11}$B, $^{13}$C, and $^{19}$F NMR spectra were recorded on a VARIAN Inova-400 (400 MHz $^{1}$H, 100 MHz $^{13}$C, 376 MHz $^{19}$F). Chemical shift values (δ) are reported in ppm (tetramethylsilane δ 0.00 ppm for $^{1}$H; trichlorofluoromethane δ 0.00 ppm for $^{19}$F; residual chloroform δ 77.0 ppm for $^{13}$C; $BF_3$•$OEt_2$ δ 0.00 ppm for $^{11}$B). Optical rotations were measured on a JASCO P-1030 digital polarimeter. GC analysis was performed with a Shimadzu model 2014 instrument using nitrogen as a carrier gas. Analytical HPLC was performed on a JASCO PU1586 with a UV-1575 UV/Vis detector using a chiral column.

**Materials:** Commercial grade reagents and solvents were used without further purification unless otherwise noted. Dry solvent, dichloromethane and THF were purchased from Kanto Chemical Co. Inc. 1,3-Cyclopentadiene was cracked at 200 ˚C (bath temp.) and distilled before use. Lewis acid-activated oxazaborolidine catalyst **1** was prepared from corresponding oxazaborolidine **20** and $SnCl_4$ according to the literature procedure (Scheme S1).[3] Ethyl (*Z*)-4,4,4-trifluorobut-2-enoate [(*Z*)-**3**][4] and ethyl (*E*)-4,4-difluorobut-2-enoate (**6**)[5] were synthesized according to reported procedures.

**Scheme S1**




**Experimental procedure for asymmetric Diels-Alder reaction and characterization of Diels-Alder adducts in Table 1**

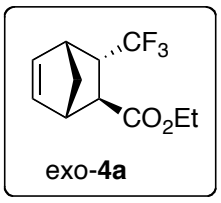
*Typical procedure for the asymmetric Diels-Alder reaction.*

To a dried Schlenk flask was charged with dichloromethane (0.4 ml) and a 0.1 M solution of oxazaborolidine **20** in dichloromethane (173.9 μl, 0.017 mmol) under argon atmosphere. After this solution was cooled to -78 ˚C, a 1.0 M solution of $SnCl_4$ (17.4 μl, 0.017 mmol) was added. The resulting solution was stirred for 15 min at this temperature. To this catalyst solution, were added cyclopentadiene (72 μl, 0.87 mmol) and dienophile (*E*)-**2** (25 μl, 0.17 mmol) successively. After the reaction mixture was stirred for 8 h at -78 ˚C, the reaction was quenched with 12 μl of $Et_3N$ (*ca*. 5 equiv for catalyst). The reaction mixture was allowed to warm to room temperature slowly. The solvent was treated with *sat*.$NaHCO_3$ *aq*. The aqueous layer was extracted with dichloromethane three times, and the combined organic extracts were dried over $Na_2SO_4$, and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane : ether = 30 : 1) to give 81% yield of **4a** as a colorless oil (exo/endo = 78/22). Each diastereomer was isolated by the second careful silica gel column chromatography as a sole diastereomer.

Racemic adducts were prepared by using $EtAlCl_2$ in dichloromethane or by heating under neat condition. Racemic **10** was synthesized by using racemic **1**.

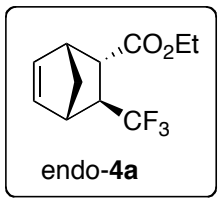
*Characterization of Diels-Alder adducts*

Relative configuration of **4a** was confirmed by comparing its NMR spectra with authentic sample, which was prepared by reported procedure.[6] Relative configuration of **5a** was confirmed by comparing its NMR spectra with reported ones.[7] Both relative and absolute stereochemistry of **5c** was confirmed by X-ray crystallographic analysis of **19** (see page S15). Stereochemistry of other Diels-Alder adducts was assigned based on NMR spectroscopic analogy with abovementioned compounds.



exo-**4a**

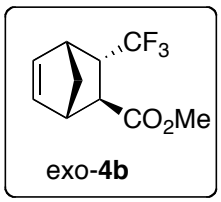
exo-**4a**[6] (99% ee): $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.29 (dd, 1H, *J* = 5.2, 3.2 Hz), 6.15-6.13 (m, 1H), 4.19 (q, 2H, *J* = 7.2 Hz), 3.27-3.18 (m, 1H), 3.18 (s, 1H), 3.11 (s, 1H) 2.34 (dd, 1H, *J* = 5.6, 1.6 Hz), 1.67 (d, 1H, *J* = 9.2 Hz), 1.49 (d, 1H, *J* = 8.8 Hz), 1.29 (t, 3H, *J* = 7.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.56, 136.93, 134.89, 127.16 (q, *J* = 275.8 Hz), 61.32, 48.32, 47.63, 46.84 (q, *J* = 26.4 Hz), 46.11 (d, *J* = 1.1 Hz), 43.45 (q, *J* = 1.9 Hz), 14.30; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -66.70 (d, *J* = 9.0 Hz); $[\alpha]^{22}_{D}$ = +53.6 (*c* = 0.275, $CHCl_3$); FTIR (neat) $\upsilon_{max}$ 3073, 2987, 1731, 1463, 1404, 1368, 1332, 1283, 1248, 1186, 1149, 1127, 1105, 1033, 1003, 984, 952, 916, 888, 875, 825, 735, 687 cm$^{-1}$; Anal. Calcd (%) for $C_{11}H_{13}F_3O_2$: C, 56.41; H, 5.59. Found: C, 56.46; H, 5.86. The enantiomeric ratio was determined by GC using a Chiral beta DEX 120 column: major isomer 60.2 min and minor isomer 52.0 min (80 ˚C isothermal).



endo-**4a**

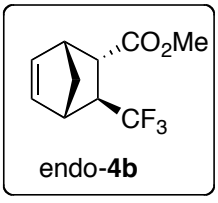
endo-**4a**[6] (99% ee): $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.35-6.32 (m, 1H), 6.09-6.07 (m, 1H), 4.16-4.10 (m, 2H), 3.29 (s, 1H), 3.07 (s, 1H), 3.02-3.00 (m, 1H) 2.57-2.48 (m, 1H), 1.73-1.48 (m, 2H), 1.25 (t, 3H, *J* = 7.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 172.38, 138.13, 135.22, 127.68 (q, *J* = 276.6 Hz), 61.11, 47.57 (q, *J* = 1.65 Hz), 46.55 (q, *J* = 27.1 Hz), 45.92, 45.80 (d, *J* = 1.0 Hz), 44.01 (q, *J* = 1.7 Hz), 14.40; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -68.02 (d, *J* = 10.1 Hz); $[\alpha]^{19}_{D}$ = +66.6 (*c* = 0.365, $CHCl_3$). The enantiomeric ratio was determined by GC using a Chiral beta DEX 120 column: major isomer 57.2 min and minor isomer 56.2 min (80 ˚C isothermal).

**4b**: The crude mixture was purified by silica gel column chromatography (hexane : ether = 30 : 1) to give 78% yield of **4b** as a diastereomixture (exo/endo = 76/24). All analytical data were obtained with a diastereomeric mixture.



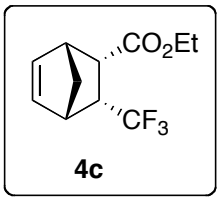
exo-**4b**

exo-**4b** (99% ee): $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.29 (dd, 1H, *J* = 5.6, 3.2 Hz), 6.15-6.13 (m, 1H), 3.75 (s, 3H), 3.28-3.19 (m, 1H), 3.15 (s, 1H), 3.11 (s, 1H), 2.36-2.34 (m, 1H), 1.67 (d, 1H, *J* = 8.8 Hz), 1.50 (d, 1H, *J* = 8.8 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 174.04, 136.86, 134.92, 127.11 (q, *J* = 276.2 Hz), 52.49, 48.29, 47.65, 46.88 (q, *J* = 26.7 Hz), 45.91 (d, *J* = 1.1 Hz), 43.44 (q, *J* = 1.9 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$) δ -66.70 (d, *J* = 9.0 Hz); $[\alpha]^{28}_{D}$ = +39.9 (*c* = 0.71, $CHCl_3$); FTIR (neat) $\upsilon_{max}$ 2990, 2957, 1738, 1437, 1401, 1334, 1283, 1250, 1150, 1127, 1106, 1023, 994, 954, 935 cm$^{-1}$; Anal. Calcd (%) for $C_{10}H_{11}F_3O_2$: C, 54.55; H, 5.04. Found: C, 54.82; H, 5.30. The enantiomeric ratio was determined by GC using a Chiral beta DEX 120 column: major isomer 26.1 min and minor isomer 23.2 min (90 ˚C isothermal).



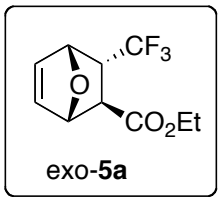
endo-**4b**

endo-**4b** (99% ee). This compound could not be isolated from exo-form: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.34 (dd, 1H, *J* = 6.0, 3.6 Hz), 6.08 (dd, 1H, *J* = 8.4, 2.8 Hz), 3.68 (s, 3H), 3.29 (brs, 1H), 3.08 (brs, 1H), 3.02 (dd, 1H, *J* = 4.8, 3.6 Hz), 2.57-2.48 (m, 1H), 1.72 (d, 1H, *J* = 9.2 Hz), 1.50 (d, 1H, *J* = 8.8 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$): δ -68.05 (d, *J* = 10.5 Hz). The enantiomeric ratio was determined by GC (90 ˚C) using a Chiral beta DEX 120 column: major isomer 25.5 min and minor isomer 24.1 min.

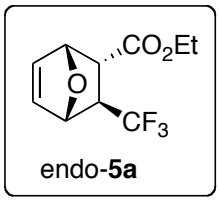



**4c** (99% ee)**:**The crude mixture was purified by silica gel column chromatography (hexane : dichloromethane = 10 : 1) to give 75% yield of **4c** as a colorless oil (99% ee): $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.48 (dd, 1H, *J* = 8.4, 2.8 Hz), 6.11-6.09 (m, 1H), 4.15-4.03 (m, 2H), 3.29-3.17 (m, 2H), 1.49 (d, 1H, *J* = 8.8 Hz), 1.31 (d, 1H, *J* = 8.8 Hz) 1.22 (t, 3H, *J* = 6.8 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 171.43, 137.57, 132.52, 126.61 (q, *J* = 277.3 Hz), 60.81, 48.36 (q, *J* = 26.3 Hz), 48.30, 47.28, 45.93, 45.03 (q, *J* = 8.6 Hz), 14.01; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -61.3 (d, *J* = 10.5 Hz); $[\alpha]^{19}_{D}$ = +26.3 (*c* = 0.445, $CHCl_3$); FTIR (neat) $\upsilon_{max}$ 2986, 2930, 1737, 1457, 1370, 1341, 1277, 1194, 1141, 1116, 1064, 1042, 982, 912, 839, 775, 747 cm$^{-1}$; Anal. Calcd (%) for $C_{11}H_{13}F_3O_2$: C, 56.41; H, 5.59. Found: C, 56.27; H, 5.65. The enantiomeric ratio was determined by GC using a Chiral beta DEX 120 column: major isomer 44.2 min and minor isomer 39.6 min (110 ˚C isothermal).

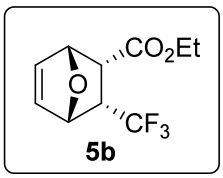
**5a:** The crude mixture was purified by silica gel column chromatography (hexane : dichloromethane = 1 : 1) to give 94% yield of **5a** as a colorless oil (exo/endo = 76/24). Each diastereomer was isolated by the second careful silica gel column chromatography as a nearly sole diastereomer.



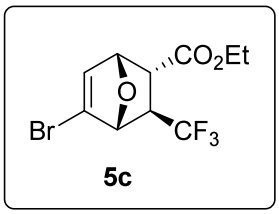

exo-**5a**[7] (99% ee): $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.58 (dd, 1H, *J* = 5.6, 1.6 Hz), 6.42-6.40 (m, 1H), 5.24 (s, 1H), 5.16-5.14 (m, 2H), 4.24 (q, 2H, *J* = 7.2 Hz), 3.44 (qdd, 1H, *J* = 9.4, 4.7, 4.7 Hz), 2.53 (d, 1H, *J* = 4.8 Hz), 1.31 (t, 3H, *J* = 7.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 171.13, 136.85, 134.35, 125.55 (q, *J* = 275.0 Hz), 83.04, 78.04 (d, *J* = 2.7 Hz), 61.85, 46.51 (q, *J* = 1.2 Hz), 46.04 (q, *J* = 27.5 Hz), 14.25; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -65.50 (d, *J* = 9.0 Hz); $[\alpha]^{17}_{D}$ = +87.8 (*c* = 0.685, $CHCl_3$); FTIR (neat) $\upsilon_{max}$ 2986, 1738, 1369, 1282, 1210, 1147, 1122, 1018, 895, 863, 710 cm$^{-1}$; Anal. Calcd (%) for $C_{10}H_{11}F_3O_3$: C, 50.85; H, 4.69. Found: C, 50.80; H, 4.84. The enantiomeric ratio was determined by GC using a Chiral beta DEX 325 column: major isomer 37.0 min and minor isomer 39.1 min (90 ˚C isothermal).




endo-**5a**[7] (99% ee): $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.55 (dd, 1H, *J* = 5.6, 1.6 Hz), 6.38 (dd, 1H, *J* = 6.0, 1.6 Hz), 5.27 (d, 1H, *J* = 4.8 Hz), 5.14 (s, 1H), 4.15 (qd, 2H, *J* = 7.2, 1.2 Hz), 3.22-3.20 (m, 1H), 2.68 (qd, 1H, *J* = 9.2, 4.8 Hz), 1.27 (t, 3H, *J* = 7.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 169.81, 136.83, 135.23, 126.80 (q, *J* = 276.6 Hz), 79.40 (q, *J* = 2.3 Hz), 79.16, 61.57, 45.59 (q, *J* = 27.4 Hz), 45.70, 14.28; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -68.55 (d, *J* = 9.5 Hz); $[\alpha]^{18}_{D}$ = +84.1 (*c* = 0.695, $CHCl_3$); FTIR (neat) $\upsilon_{max}$ 2994, 1724, 1357, 1313, 1281, 1189, 1114, 1032, 995, 892, 734 cm$^{-1}$; Anal. Calcd (%) for $C_{10}H_{11}F_3O_3$: C, 50.85; H, 4.69. Found: C, 50.41; H, 4.77. The enantiomeric ratio was determined by GC using a Chiral beta DEX 325 column: major isomer 42.5 min and minor isomer 38.6 min (90 ˚C isothermal).



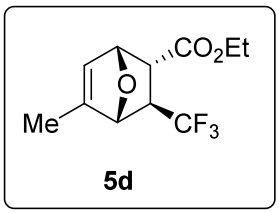

**5b**[8] (99% ee)**:** The crude mixture was purified by silica gel column chromatography (hexane : ethyl acetate= 8 : 1) to give 67% yield of **5b** as a yellow solid (99% ee).: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.79 (dd, 1H, *J* = 6.0, 2.0 Hz), 6.42-6.39 (m, 1H), 5.15-5.09 (m, 2H), 4.18-4.05 (m, 2H), 3.44-3.30 (m, 2H), 1.23 (t, 3H, *J* = 7.6 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 169.54 137.97, 132.89, 125.14 (q, *J* = 276.6 Hz), 79.98 (d, *J* = 4.9 Hz), 78.90, 61.26, 47.40 (q, *J* = 27.4 Hz), 46.67, 29.85, 13.95; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -61.28 (d, *J* = 9.0 Hz); $[\alpha]^{26}_{D}$ = +7.1 (*c* = 0.455, $CHCl_3$); FTIR (neat) $\upsilon_{max}$ 2976, 2925, 1736, 1467, 1371, 1343, 1323, 1295, 1272, 1198, 1122, 1052, 1030, 947, 900 cm$^{-1}$; Anal. Calcd (%) for $C_{10}H_{11}F_3O_3$: C, 50.85; H, 4.69. Found: C, 50.87; H, 5.08. The enantiomeric ratio was determined by GC using a Chiral beta DEX 325 column: major isomer 24.7 min and minor isomer 27.3 min (110 ˚C isothermal).



**5c**

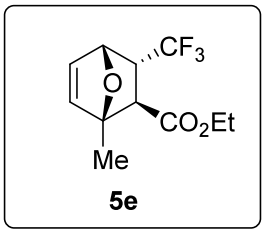
**5c** (99% ee)**:** The crude mixture was purified by silica gel column chromatography (hexane : ethyl acetate = 2 : 1) to give 89% yield of **5c** as a colorless oil (99% ee). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.42 (d, 1H, *J* = 2.0 Hz), 5.22 (d, 1H, *J* = 4.8 Hz), 4.95 (s, 1H), 4.17 (q, 2H, *J* = 7.2 Hz), 3.28-3.26 (m, 1H), 2.85 (qd, 1H, *J* = 9.2, 4.4 Hz), 1.27 (t, 3H, *J* = 7.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 169.19, 134.36, 127.03, 126.25 (q, *J* = 276.6 Hz), 84.13 (d, *J* = 2.6 Hz), 81.27, 61.81, 47.38, 46.54 (q, *J* = 28.6 Hz), 14.21; .$^{19}$F NMR (376 MHz, $CDCl_3$) δ -68.42 (d, *J* = 8.3 Hz); $[\alpha]^{21}_{D}$ = +96.6 (*c* = 1.04, $CHCl_3$); FTIR (neat) $\upsilon_{max}$ 3153, 3088, 2985, 1739, 1583, 1448, 1393, 1369, 1331, 1281, 1212, 1152, 1125, 1050, 1011, 970, 918, 901, 876, 837, 757 cm$^{-1}$; Anal. Calcd (%) for $C_{10}H_{10}BrF_3O_3$: C, 38.12; H, 3.20. Found: C, 37.95; H, 3.18. The enantiomeric ratio was determined by GC using a Chiral B-DA column: major isomer 70.4 min and minor isomer 68.9 min (90 ˚C isothermal).

Both relative and absolute stereochemistry was determined by X-ray crystallographic analysis of **23** (see page S15).



**5d**

**5d** (99% ee)**:** The crude mixture was purified by silica gel column chromatography (hexane : dichloromethane = 2 : 1) to give 80% yield of **5d**, along with minor diastereomer, as a colorless oil (99% ee). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 5.89-5.88 (m, 1H), 5.15 (d, 1H, *J* = 4.4 Hz), 4.83 (q, 2H, *J* = 7.2 Hz), 3.24-3.22 (m, 1H), 2.66 (qd, 1H, *J* = 9.6, 4.4 Hz), 1.90-1.89 (m, 3H), 1.26 (t, 3H, *J* = 7.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 169.97, 147.64, 128.17, 126.91 (q, *J* = 276.6 Hz), 82.60 (d, *J* = 2.3 Hz), 80.16, 61.42, 47.84, 46.16 (q, *J* = 24.2 Hz), 14.24, 12.36; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -68.4 (d, *J* = 9.0 Hz); $[\alpha]^{21}_{D}$ = +118.9 (*c* = 0.350, $CHCl_3$); FTIR (neat) $\upsilon_{max}$ 2983, 2942, 2915, 1739, 1636, 1446, 1391, 1369, 1333, 1282, 1208, 1148, 1119, 1064, 1044, 1017, 998, 973, 959, 909, 879, 864 cm$^{-1}$; Anal. Calcd (%) for $C_{11}H_{13}F_3O_3$: C, 52.80; H, 5.24. Found: C, 52.36; H, 5.21. The enantiomeric ratio was determined by GC using a Chiral B-DA column: major isomer 19.9 min and minor isomer 20.5 min (100 ˚C isothermal).

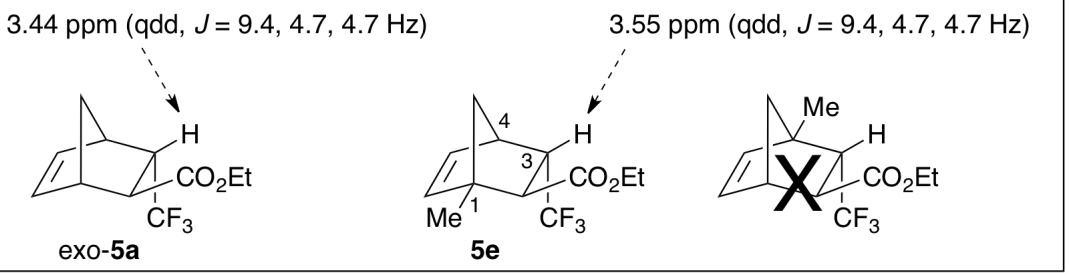


**5e**

**5e** (99% ee)**:**The crude mixture was purified by silica gel column chromatography (hexane : dichloromethane = 3 : 1) to give 99% yield of **5e** as a colorless oil (99% ee). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.40-6.39 (m, 1H), 6.35 (d, 1H, *J* = 5.6 Hz), 5.09 (dd, 1H, *J* = 4.4, 1.6 Hz), 4.32-4.18 (m, 2H), 3.55 (qdd, 1H, *J* = 9.4, 4.7, 4.7 Hz), 2.52 (d, 1H, *J* = 5.2 Hz), 1.59 (s, 3H), 1.32 (t, 3H, *J* = 7.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) 90.21, 77.52 (q, *J* = 2.3 Hz), 61.56, 49.28, 48.87 (q, *J* = 27.1 Hz), 16.14, 14.41; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -66.04 (d, *J* = 9.0 Hz); $[\alpha]^{15}_{D}$ = +71.3 (*c* = 0.445, $CHCl_3$); FTIR (neat) $\upsilon_{max}$ 2984, 1735, 1456, 1394, 1326, 1281, 1212, 1121, 1025, 959, 864, 716 cm$^{-1}$; Anal. Calcd (%) for $C_{11}H_{13}F_3O_3$: C, 52.80; H, 5.24. Found: C, 52.83; H, 5.26. The enantiomeric ratio was determined by GC using a Chiral beta DEX 120 column: major isomer 23.4 min and minor isomer 24.1 min (100 ˚C isothermal).

Regiochemistry of **5e** was confirmed by $^{1}$H NMR analysis. As shown in Figure S4, the spin-spin coupling pattern of hydrogen at C-3 of **5e** was completely the same as that of exo-**5a** (qdd, *J* = 9.6, 4.8, 4.8 Hz). Therefore, we concluded that the methyl group of **5e** is attached to C(1), not to C(4).

**Figure S4.**

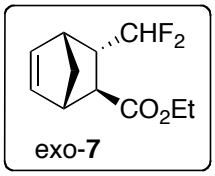



**Characterization of Diels-Alder adducts in Table 2**

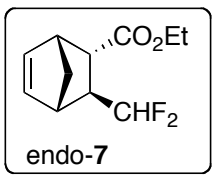
Diels-Alder reaction was performed with ethyl (*E*)-4,4-difluorobut-2-enoate (**6**)[5] in accordance with typical procedure (see page S3).

Stereochemistry of Diels-Alder adducts was estimated by analogy with corresponding $CF_3$-cyclohexenes.

**7:** The crude mixture was purified by silica gel column chromatography (hexane : dichloromethane = 2 : 1) to give 90% yield of **7** as a colorless oil (exo/endo = 57/43). Each diastereomer was isolated by the second careful silica gel column chromatography as a sole diastereomer.

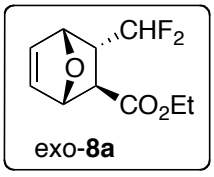



*exo*-**7:** (99% ee): $^1$H NMR (400 MHz, $CDCl_3$) δ 6.32-6.30 (m, 1H), 6.17-6.15 (m, 1H), 5.25 (td, 1H, *J* = 57.0, 8.2 Hz), 4.18 (q, 2H, *J* = 7.2 Hz), 3.10 (s, 1H), 3.06 (s, 1H) 2.98-2.88 (m, 1H), 2.13 (t, 3H, *J* = 4.8 Hz), 1.72-1.46 (m, 1H), 1.28 (t, 3H, *J* = 7.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 174.03 137.96, 134.94, 119.58 (t, *J* = 238.9 Hz), 61.11, 47.98 (dd, *J* = 22.9, 19.0 Hz), 47.76, 47.32, 45.44 (d, *J* = 7.2 Hz), 43.31 (d, *J* = 7.6 Hz), 14.32; .$^{19}$F NMR (376 MHz, $CDCl_3$) δ -114.30 (ddd, *J* = 287.3, 59.8, 10.5 Hz), -119.88 (dddd, *J* = 283.5, 56.0, 12.4, 3.4 Hz); $[\alpha]^{27}_D$ = +13.3 (*c* = 0.600, $CHCl_3$); FTIR (neat) $\upsilon_{max}$ 2984, 1730, 1373, 1336, 1256, 1191, 1100, 1063, 1030, 935 cm$^{-1}$; Anal. Calcd (%) for $C_{11}H_{14}F_2O_2$: C, 61.10; H, 6.53. Found: C, 61.11; H, 6.50. The enantiomeric ratio was determined by GC using a Chiral beta DEX 325 column: major isomer 37.2 min and minor isomer 36.1 min (100 ˚C isothermal).




*endo*-**7:** (99% ee): $^1$H NMR (400 MHz, $CDCl_3$) δ 6.32-6.30 (m, 1H), 6.09-6.07 (m, 1H), 5.85 (td, 1H, *J* = 56.4, 4.6 Hz), 4.15-4.07 (m, 2H), 3.26 (s, 1H), 2.98 (s, 1H) 2.89(dd, 1H, *J* = 5.2, 3.6 Hz), 2.31-2.20 (m, 1H), 1.24 (t, 3H, *J* = 7.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.00, 138.14, 134.98, 118.10 (t, *J* = 240.4 Hz), 60.85, 47.22, 46.82 (t, *J* = 19.8 Hz), 45.71, 45.26 (t, *J* = 2.6 Hz), 43.23 (t, *J* = 3.8 Hz), 14.36; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -117.58 (ddd, *J* = 280.5, 57.2, 17.3 Hz), -119.32 (ddd, *J* = 280.1, 57.2, 14.7 Hz); $[\alpha]^{27}_D$ = +76.3 (*c* = 0.600, $CHCl_3$); FTIR (neat) $\upsilon_{max}$ 2984, 1735, 1462, 1375, 1334, 1265, 1193, 1134, 1112, 1055, 862 cm$^{-1}$; Anal. Calcd (%) for $C_{11}H_{14}F_2O_2$: C, 61.10; H, 6.53. Found: C, 61.13; H, 6.50. The enantiomeric ratio was determined by GC using a Chiral beta DEX 325 column: major isomer 40.7 min and minor isomer 41.6 min (100 ˚C isothermal).

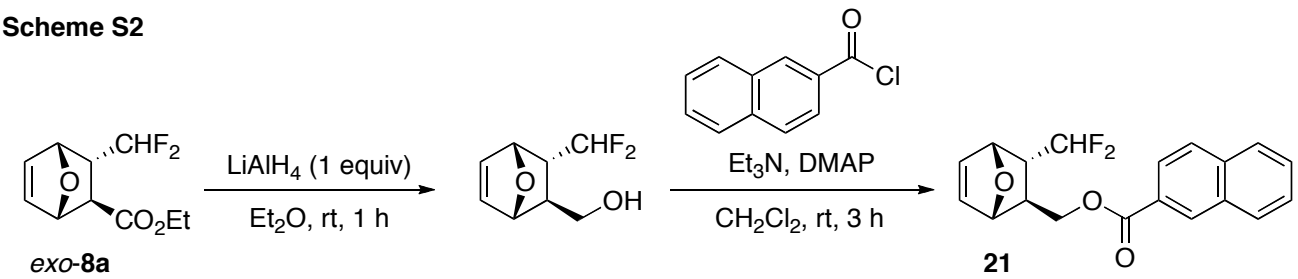
**8:** The crude mixture was purified by silica gel column chromatography (hexane : dichloromethane = 2 : 1) to give 99% yield of **8** as a colorless oil (exo/endo = 53/47). Each diastereomer was isolated by the second careful silica gel column chromatography as a sole diastereomer.




*exo*-**8a:** (99% ee): $^1$H NMR (400 MHz, $CDCl_3$) δ 6.57 (dd, 1H, *J* = 6.0, 2.0 Hz), 6.47-6.45 (m, 1H), 5.38 (td, 1H, *J* = 56.8, 7.6 Hz), 5.23 (s, 1H), 5.10-5.09 (m, 1H), 4.22 (q, 2H, *J* = 7.2 Hz) 3.22-3.12 (m, 1H), 2.34-2.33 (m, 1H), 1.30 (t, 3H, *J* = 7.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 171.64, 137.19, 134.52, 117.75 (t, *J* = 238.1 Hz), 82.25, 78.24 (dd, *J* = 8.5, 1.9 Hz), 61.62, 47.04 (dd, *J* = 23.3, 20.6 Hz), 45.57 (d, *J* = 6.5 Hz), 14.24; $^{19}$F NMR (376 MHz, $CDCl_3$) δ

-115.20 (ddd, $J$ = 292.9, 57.2, 11.3 Hz), -117.5 (ddd, $J$ = 291.8, 56.0, 12.4 Hz); $[\alpha]^{28}_{D}$ = +49.3 ($c$ = 0.595, $CHCl_3$); FTIR (neat) $\upsilon_{max}$ 2986, 1726, 1375, 1321, 1266, 1230, 1187, 1103, 1056, 1020, 961, 899 $cm^{-1}$; Anal. Calcd (%) for $C_{10}H_{12}F_2O_3$: C, 55.05; H, 5.54. Found: C, 54.98; H, 5.56. The enantiomeric ratio was determined by HPLC analysis after converted into corresponding naphthoate **21** (see Scheme S2).

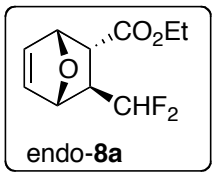
**Scheme S2**




*exo*-**8a** **21**

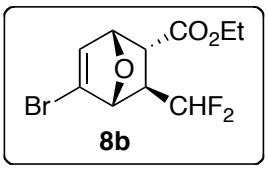
To a solution of *exo*-**8a** (57.6 mg, 0.26 mmol) in ether (5 ml) was added $LiAlH_4$ (10.5 mg, 0.27 mmol) at 0 ˚C under argon atmosphere. The mixture was allowed to warm to room temperature and stirred for 1 h. The mixture was then poured into $NH_4Cl$ aq at 0 ˚C. The organic layer was extracted with water two times, and the organic extracts was dried over $Na_2SO_4$, and concentrated in *vacuo*. The crude mixture was immediately subjected to the next reaction without purification.

To a solution of this crude alcohol in dry dichloromethane (2 ml), were added 2-naphthoyl chloride (35.7 mg, 0.186 mmol), $Et_3N$ (39.5 μl, 0.279 mmol) and DMAP (0.009 mmol) at 0 ˚C under argon atmosphere. The mixture was allowed to warm to room temperature and stirred for 3 h. The mixture was then poured into $NaHCO_3$ aq at 0 ˚C. The aqueous layer was extracted with dichloromethane three times, and the combined organic extracts was dried over $Na_2SO_4$, and concentrated in *vacuo*. The crude mixture was purified by silica gel column chromatography (hexane : ethyl acetate = 1 : 1) to give 67% yield of **21** as a white solid (99% ee). **21**: $^1$H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.07 (dd, 1H, $J$ = 8.4, 1.6 Hz), 7.97 (d, 1H, $J$ = 8.4 Hz), 7.90-7.88 (m, 2H), 7.62-7.53 (m, 2H), 6.59 (dd, 1H, $J$ = 6.0, 1.6 Hz), 6.44 (d, 1H, $J$ = 5.6 Hz) 5.35 (td, 1H, $J$ = 56.4, 7.6 Hz), 5.06 (d, 1H, $J$ = 4.4 Hz), 4.98 (s, 1H), 4.52-4.43 (m, 2H), 2.50-2.41 (m, 1H), 2.08-2.04 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.65, 137.59, 135.74, 133.65, 132.61, 131.36, 129.54, 128.50, 128.37, 127.92, 127.27, 126.84, 125.30, 118.39 (t, $J$ = 238.1 Hz), 80.46, 78.30 (dd, $J$ = 9.3, 1.3 Hz), 66.55, 47.64 (dd, $J$ = 22.9, 20.2 Hz), 40.34 (d, $J$ = 6.9 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$) δ -113.48 (ddd, $J$ = 290.7, 56.0, 7.90 Hz), -116.68 (ddd, $J$ = 291.8, 56.0, 13.9 Hz); $[\alpha]^{19}_{D}$ = +13.5 ($c$ = 0.430, $CHCl_3$); FTIR (neat) $\upsilon_{max}$ 3060, 3004, 2955, 1715, 1631, 1599, 1576, 1508, 1468, 1407, 1390, 1354, 1317, 1284, 1227, 1197, 1131, 1111, 1064, 1017, 964, 913, 871, 831, 779 $cm^{-1}$; Anal. Calcd (%) for $C_{19}H_{16}F_2O_3$: C, 69.08; H, 4.88. Found: C, 69.21; H, 5.34. The enantiomeric ratio was determined by HPLC (hexane : 2-propanol = 50 : 1, 1.0 mL/min) using a CHIRALPAK IC column (0.46 cmϕ x 25 cm): major isomer 37.0 min and minor isomer 38.8 min.

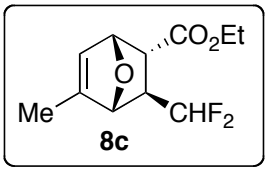



endo-**8a**

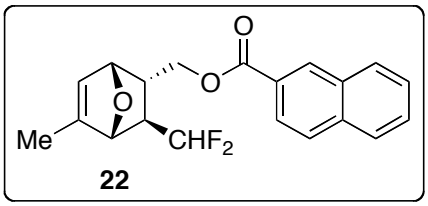
*endo*-**8a:** (99% ee): $^1$H NMR (400 MHz, $CDCl_3$) δ 6.51 (dd, 1H, $J$ = 6.0, 2.0 Hz), 6.36 (dd, 1H, $J$ = 6.0, 1.6 Hz), 5.74 (td, 1H, $J$ = 56.4, 6.8 Hz), 5.23-5.22 (m, 1H), 5.03 (s, 1H), 4.16-4.10 (m, 2H) 3.03-3.00 (m, 1H), 2.51-2.42 (m, 1H), 1.25 (t, 3H, $J$ = 7.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.26, 136.46, 134.99, 117.99 (t, $J$ = 240.8 Hz), 79.52 (dd, $J$ = 8.0, 2.2 Hz), 79.38, 61.30, 46.99 (dd, $J$ = 24.1, 19.5 Hz), 45.71 (d, $J$ = 6.1 Hz), 14.26; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -116.63 (ddd, $J$ = 283.9, 57.5, 13.9 Hz), -120.27 (ddd, $J$ = 282.8, 56.0, 10.5 Hz); $[\alpha]^{28}_{D}$ = +64.2 ($c$ = 0.510, $CHCl_3$); FTIR (neat) $\upsilon_{max}$ 2984, 1738, 1448, 1372, 1315, 1285, 1205, 1132, 1099, 1054, 980, 945, 926, 902, 869 $cm^{-1}$; Anal. Calcd (%) for $C_{10}H_{12}F_2O_3$: C, 55.05; H, 5.54. Found: C, 54.68; H, 5.62. The enantiomeric ratio was determined by GC using a Chiral beta DEX 120 column: major isomer 29.4 min and minor isomer 33.3 min (110 ˚C isothermal).



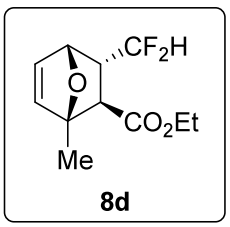

**8b** (99% ee)**:** The crude mixture was purified by silica gel column chromatography (hexane : dichloromethane = 2 : 3) to give 72% yield of **8b** as a colorless oil: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.41 (d, 1H, *J* = 1.6 Hz), 5.77 (td, 1H, *J* = 56.4, 6.4 Hz), 5.19-5.18 (m, 1H), 4.85 (s, 1H), 4.18-4.13 (m, 2H), 3.11-3.09 (m, 1H), 2.67-2.59 (m, 1H), 1.24 (t, 3H, *J* = 6.8 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 169.70, 134.11, 126.82, 117.13 (t, *J* = 241.5 Hz), 84.17 (dd, *J* = 8.0, 2.7 Hz), 81.48, 61.59, 47.26 (d, *J* = 5.3 Hz), 46.86 (dd, *J* = 23.6, 20.9 Hz), 14.26; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -116.91 (ddd, *J* = 285.0, 56.0, 12.8 Hz), -120.43 (ddd, *J* = 283.9, 56.4, 10.5 Hz); $[\alpha]^{20}_{D}$ = +105.2 (*c* = 0.485, $CHCl_3$); FTIR (neat) $\upsilon_{max}$ 2983, 1738, 1583, 1447, 1373, 1281, 1211, 1132, 1047, 957, 903, 866 $cm^{-1}$ $cm^{-1}$; Anal. Calcd (%) for $C_{10}H_{11}BrF_2O_3$: C, 40.43; H, 3.73. Found: C, 40.68; H, 3.78. The enantiomeric ratio was determined by GC using a Chiral beta DEX 225 column: major isomer 136.3 min and minor isomer 132.6 min (100 ˚C isothermal).




**8c** (99% ee)**:** The crude mixture was purified by silica gel column chromatography (hexane : dichloromethane = 1 : 2) to give 87% yield of **8c** as a colorless oil: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.57 (dd, 1H, *J* = 6.0, 2.0 Hz), 6.47-6.45 (m, 1H), 5.38 (td, 1H, *J* = 56.8, 7.6 Hz), 5.23 (s, 1H), 5.10-5.09 (m, 1H), 4.22 (q, 2H, *J* = 7.2 Hz) 3.22-3.12 (m, 1H), 2.34-2.33 (m, 1H), 1.30 (t, 3H, *J* = 7.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.39, 147.28, 127.90, 118.11 (t, *J* = 240.7 Hz), 82.74 (dd, *J* = 7.6, 1.9 Hz), 80.43, 61.19, 47.80 (d, *J* = 6.1 Hz), 46.55 (dd, *J* = 23.7, 19.5 Hz), 14.28, 12.50; .$^{19}$F NMR (376 MHz, $CDCl_3$) δ -116.23 (ddd, *J* = 283.9, 57.2, 13.5 Hz), -120.0 (ddd, *J* = 283.9, 56.0, 10.5 Hz); $[\alpha]^{18}_{D}$ = +88.6 (*c* = 0.505, $CHCl_3$); FTIR (neat) $\upsilon_{max}$ 2982, 1738, 1635, 1446, 1373, 1350, 1284, 1204, 1155, 1123, 1062, 1037, 965, 942, 906, 867, 785 $cm^{-1}$; Anal. Calcd (%) for $C_{11}H_{14}F_2O_3$: C, 56.89; H, 6.08. Found: C, 57.03; H, 6.06. The enantiomeric ratio was determined by HPLC analysis after converted into corresponding naphthoate **22**. Naphthoate **22** was synthesized according to the procedure shown in Scheme S2.



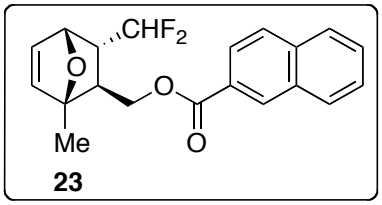

The crude mixture was purified by silica gel column chromatography (hexane: dichlromethane = 1 : 4) to give 92% yield of **22** as a colorless oil (99% ee). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.05 (dd, 1H, *J* = 8.4, 1.6 Hz), 7.97 (s, 1H), 7.91-7.89 (m, 2H), 7.63-7.54 (m, 2H), 6.05-6.04 (m, 1H), 5.77 (td, 1H, *J* = 56.8, 7.6 Hz), 5.03 (s, 1H), 4.71 (s, 1H), 4.26 (dd, 1H, *J* = 11.2, 6.8 Hz), 4.13 (dd, 1H, *J* = 11.2, 8.8 Hz), 2.71-2.65 (m, 1H), 1.92 (d, 3H, *J* = 1.6 Hz), 1.79-1.71 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.60, 146.88, 135.77, 132.61, 131.37, 129.54, 128.57, 128.43, 127.94, 127.83, 127.13, 126.90, 125.24, 118.67 (t, *J* = 239.9 Hz), 82.35 (dd, *J* = 9.2, 1.3 Hz), 80.83, 66.10, 47.08 (dd, *J* = 22.5, 9.0 Hz), 42.74 (d, *J* = 6.1 Hz), 12.62; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -114.12 (ddd, *J* = 282.4, 57.2, 11.3 Hz), -119.92 (ddd, *J* = 282.75, 68.4, 11.7 Hz); $[\alpha]^{15}_{D}$ = +61.8 (*c* = 0.560, $CHCl_3$); FTIR (neat) $\upsilon_{max}$ 3061, 2930, 2856, 1715, 1632, 1599, 1508, 1468, 1391, 1354, 1284, 1227, 1196, 1131, 1062, 1012, 976, 910, 865, 829, 780 $cm^{-1}$; Anal. Calcd (%) for $C_{20}H_{18}F_2O_3$: C, 69.76; H, 5.27. Found: C, 69.48; H, 5.75. The enantiomeric ratio was determined by HPLC (hexane : 2-propanol = 30 : 1, 1.0 mL/min) using a CHIRALPAK IC column (0.46 cmϕ x 25 cm): major isomer 16.3 min and minor isomer 23.6 min.




**8d** (99% ee)**:** The crude mixture was purified by silica gel column chromatography (hexane : dichloromethane = 1 : 3) to give 74% yield of **8d** as a colorless oil: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.44 (brd, 1H, *J* = 6.0 Hz), 6.35 (d, 1H, *J* = 5.6 Hz), 5.33 (td, 1H, *J* = 56.4, 7.2 Hz), 5.03 (dd, 1H, *J* = 4.4, 1.6 Hz), 4.31-4.16 (m, 2H), 3.34-3.24 (m, 1H), 2.34 (d, 1H, *J* = 4.4 Hz), 1.58 (s, 3H), 1.31 (t, 3H, *J* = 7.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 171.53, 140.92, 134.82, 117.80 (t, *J* = 239 Hz), 89.51, 77.91 (dd, *J* = 8.8, 1.9

Hz), 61.36, 50.11 (dd, $J$ = 23.7, 20.2 Hz), 48.68 (d, $J$ = 6.9 Hz), 16.09, 14.41; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -115.01 (ddd, $J$ = 292.9, 56.4, 10.5 Hz), -117.74 (ddd, $J$ = 291.78, 56.02, 12.41 Hz); $[\alpha]^{15}_D$ = +63.3 ($c$ = 0.405, $CHCl_3$); FTIR (neat) $\upsilon_{max}$ 2983, 1731, 1459, 1384, 1270, 1190, 1067, 860, 732 cm$^{-1}$; Anal. Calcd (%) for $C_{11}H_{14}F_2O_3$: C, 56.89; H, 6.08. Found: C, 56.83; H, 6.12.

Regiochemistry was confirmed by analogy with **5e**. The enantiomeric ratio was determined by HPLC analysis after converted into corresponding naphthoate **23**. Naphthoate **23** was synthesized according to the procedure shown in Scheme S2.



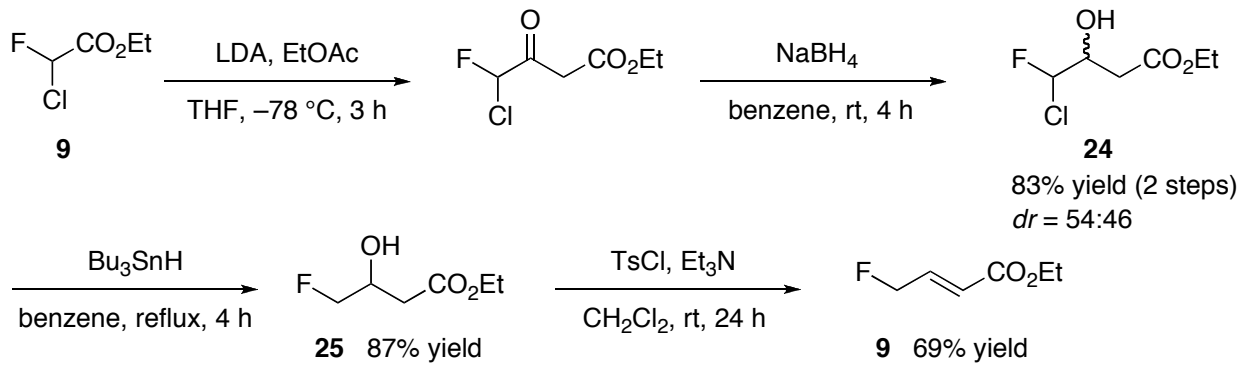
**23**

The crude mixture was purified by silica gel column chromatography (hexane: ethyl acetate = 6 : 1) to give 71% yield of **23** as a colorless oil (99% ee). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.07 (dd, 1H, $J$ = 8.4, 1.6 Hz), 7.96 (d, 1H, $J$ = 8.0 Hz), 7.90-7.89 (m, 2H), 7.62-7.53 (m, 2H), 6.44 (brd, 1H, $J$ = 5.6 Hz), 6.38 (dd, 1H, $J$ = 6.0 Hz), 5.39 (td, 1H, $J$ = 56.4, 7.6 Hz), 4.95 (dd, 1H, $J$ = 4.4, 1.2 Hz), 4.61 (dd, 1H, $J$ = 11.2, 7.2 Hz), 4.37 (dd, 1H, $J$ = 11.2, 7.2 Hz), 2.64-2.54 (m, 1H), 2.05-2.01 (m, 1H), 1.67 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.70, 141.38, 135.73, 134.10, 132.63, 131.38, 129.58, 128.49, 128.38, 127.91, 127.30, 126.82, 125.28, 118.48 (t, $J$ = 239.2 Hz), 87.80, 77.84 (dd, $J$ = 9.1, 1.5 Hz), 65.47, 50.21 (dd, $J$ = 22.2, 19.9 Hz), 41.83 (d, $J$ = 6.8 Hz), 15.91; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -113.97 (ddd, $J$ = 291.8, 56.0, 9.0 Hz), -116.85 (ddd, $J$ = 291.8, 57.5, 13.9 Hz); $[\alpha]^{24}_D$ = -8.73 ($c$ = 0.620, $CHCl_3$); FTIR (neat) $\upsilon_{max}$ 2973, 1717, 1464, 1394, 1282, 1227, 1195, 1122, 1064, 864, 772 cm$^{-1}$; Anal. Calcd (%) for $C_{20}H_{18}F_2O_3$: C, 69.76; H, 5.27. Found: C, 69.77; H, 5.25. The enantiomeric ratio was determined by HPLC (hexane : 2-propanol = 40 : 1, 1.0 mL/min) using a CHIRALPAK IC column (0.46 cmϕ x 25 cm): major isomer 24.5 min and minor isomer 31.6 min.

**Synthetic method for β-monofluoromethylacrylate (9) and characterization of Diels-Alder adduct 10 (Scheme 2)**

*Synthesis of ethyl β-monofluoromethylacrylate (**9**)*[6,9]

**Scheme S3**




To a solution of diisopropylamine (2.68 g, 26.4 mmol) in dry THF (7 ml), a 1.6 M solution of *n*-butyl lithium in hexane (3.72 ml, 26.4 mmol) was added at -40 ˚C, under argon atmosphere. The temperature was allowed to increase slowly until 0 ˚C over 1 h, then the flask was cooled again to -78 ˚C and a solution of EtOAc (2.59 ml, 26.4 mmol) in THF (2 ml) was added. After 1 h, a solution of ethyl 2-chloro-2-fluoroacetate **9** (1.5 ml, 13.2 mmol) in THF (3 ml) was added. The reaction mixture was stirred at -78 ˚C for 3 h, and after that time it was allowed to warm to rt, then the reaction was quenched with saturated aqueous $NH_4Cl$, and extracted two times with EtOAc. The organic layer was washed with 1.2 N HCl, brine, dried over $Na_2SO_4$, and then the solvent was removed in vacuo affording desired β–keto ester. This crude material was used without further purification for the next step.

To a solution of this crude material in benzene (42 ml), was added $NaBH_4$ (0.55 g, 14.5 mmol) at 0 ˚C under argon atmosphere. The mixture was allowed to warm to room temperature and stirred for 3.5 h. The mixture was then poured into 1.2N HCl *aq* at 0 ˚C. The aqueous layer was extracted with EtOAc two times, and the combined organic extracts was dried over $Na_2SO_4$, and concentrated in vacuo. The crude product was purified by silica gel column chromatography (hexane: ether = 1 : 2) to give 83% yield of **24** as a yellow oil (diastereomixture; dr = 54/46): $^1$H NMR (400 MHz, $CDCl_3$): [major isomer] δ 6.18 (dd, 1H, *J* = 50.2, 3.7 Hz), 4.42-4.32 (m, 1H), 4.21 (q, 2H, *J* = 7.2 Hz), 3.25 (brs, OH), 2.83-2.63 (m, 2H), 1.29 (t, 3H, *J* = 7.2 Hz); [minor isomer] δ 6.19 (dd, 1H, *J* = 50.0, 4.5 Hz), 4.36-4.26 (m, 1H), 4.21 (q, 2H, *J* = 7.2 Hz), 3.35 (brs, OH), 2.83-2.63 (m, 2H), 1.29 (t, 3H, *J* = 7.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$): [major isomer] δ 171.41, 102.17 (d, *J* = 243.4 Hz), 70.62 (d, *J* = 23.3 Hz), 61.44, 35.81, 14.24; [minor isomer] δ 171.58, 102.31 (d, *J* = 245.3 Hz), 71.13 (d, *J* = 22.1 Hz), 61.46, 35.18, 14.24; $^{19}$F NMR (376 MHz, $CDCl_3$): [major isomer] δ –145.5 (ddd, *J* = 50.1, 11.3, 2.2 Hz); [minor isomer]: δ 147.0 (ddd, *J* = 50.1, 13.6, 2.2 Hz)

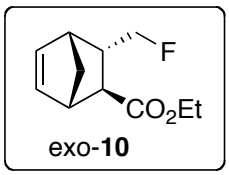
To a solution of **24** (1.0 g, 5.5 mmol) and tributyltin hydride (1.6 ml, 6.1 mmol) in dry benzene (7 ml) was added AIBN (90 mg, 0.55 mmol) under argon atmosphere. After 3.5 h refluxed, the reaction mixture was evaporated and the residue was purified by silica gel column chromatography (hexane : ether = 2 : 1) to give 87% yield of **25** as a yellow oil: $^1$H NMR (400 MHz, $CDCl_3$) δ 4.51-4.24 (m, 3H), 4.17 (q, 2H, *J* = 7.2 Hz), 3.79 (d, 1H, *J* = 4.8 Hz), 2.56 (d, 2H, *J* = 6.4 Hz), 1.28 (t, 3H, *J* = 7.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 171.72, 85.49 (d, *J* = 169.4 Hz), 66.70 (d, *J* = 20.2 Hz), 60.83, 36.97 (d, *J* = 6.1 Hz), 13.92; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -230.44 (td, *J* = 47.0, 19.6 Hz).

To a solution of **25** (551 mg, 3.7 mmol) in dry dichloromethane (3 ml), were added TsCl (1.4 g, 7.3 mmol) and $Et_3N$ (1.54 ml, 11.1 mmol) at 0 ˚C under argon atmosphere. The mixture was allowed to warm to room temperature and stirred for 24 h. The mixture was then poured into 3.0N HCl aq at 0 ˚C. The aqueous layer was extracted with dichloromethane three times, and the combined organic extracts was dried over $Na_2SO_4$, and concentrated in *vacuo*. The crude product was purified by silica gel chromatography (pentane : dichloromethane = 1.5 : 1) to give 69% yield of **9** as a colorless oil: $^1$H NMR (400 MHz, $CDCl_3$) δ 7.02-6.91 (m, 1H), 6.14-6.09 (m, 1H), 5.06 (ddd, 2H, *J* = 46.0, 3.6, 2.0 Hz), 4.23 (q, 2H, *J* = 7.2 Hz), 1.31 (t, 3H, *J* = 7.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.88, 141.54 (d, *J* = 15.6 Hz), 121.49 (d, *J* = 11.5 Hz), 81.2 (d, *J* = 170.6 Hz), 60.75, 14.30; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -223.7 (td, *J* = 48.1, 22.9 Hz).

*Diels-Alder reaction of **9** with cyclopentadiene.*

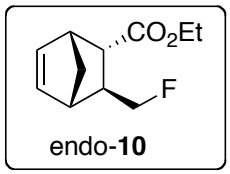
Diels-Alder reaction of **9** was performed in accordance with typical procedure (see page S3).

The crude mixture was purified by silica gel column chromatography (hexane : dichloromethane = 1.5 : 1) to give 99% yield of **10** as a diastereomeric mixture (exo/endo = 33/67). All analytical data were obtained with a diastereomeric mixture.



exo-**10**

exo-**10** (99% ee): $^1$H NMR (400 MHz, $CDCl_3$) δ 6.25 (dd, 1H, *J* = 5.6, 3.2 Hz), 6.13 (dd, 1H, *J* = 5.6, 2.8 Hz), 4.37-3.98 (m, 4H), 3.01 (brd, 1H, *J* = 1.6 Hz), 3.01 (brs, 1H), 2.82-2.73 (m, 1H), 1.72 (dd, 1H, *J* = 4.8, 1.6 Hz), 1.70-1.45 (m, 2H), 1.27 (t, 3H, *J* = 7.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 174.96, 137.26, 135.11, 86.01 (d, *J* = 166.8 Hz), 60.82, 46.85, 45.98 (d, *J* = 6.9 Hz), 45.39, 44.79 (d, *J* = 19.9 Hz), 43.56 (d, *J* = 3.4 Hz), 14.37; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -215.70 (tdd, *J* = 47.0, 10.2, 2.3 Hz).



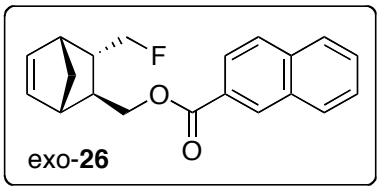
endo-**10**

endo-**10** (99% ee): $^1$H NMR (400 MHz, $CDCl_3$) δ 6.29 (dd, 1H, *J* = 5.6, 3.2 Hz), 6.07 (dd, 1H, *J* = 5.6, 2.8 Hz), 4.69-4.53 (m, 1H), 4.49-4.33 (m, 1H), 4.13-4.04 (m, 2H), 3.19 (brs, 1H), 2.84 (brd, 1H, *J* = 1.2 Hz), 2.54 (dd, 1H, *J* = 5.2, 3.6 Hz), 2.19-2.09 (m, 1H), 1.70-1.45 (m, 2H), 1.24 (t, 3H, *J* = 7.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.72, 138.30, 134.45, 86.06 (d, *J* = 169.0 Hz), 60.56, 47.60, 46.58 (d, *J* = 5.7 Hz), 46.48, 44.44 (d, *J* = 2.6 Hz), 44.09 (d, *J* = 19.1 Hz), 14.37; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -217.08 (td, *J* = 47.0, 18.4

Hz); The enantiomeric ratio was determined by GC using a Chiral beta DEX 120 column: major isomer 80.2 min and minor isomer 82.1 min (100 °C isothermal).

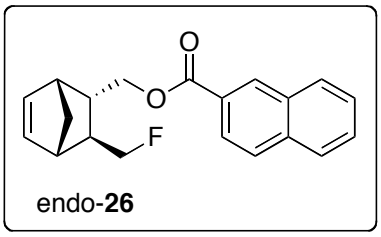
FTIR (neat) $\upsilon_{max}$ 2975, 1730, 1464, 1378, 1246, 1185, 1009, 725 $cm^{-1}$; Anal. Calcd (%) for $C_{11}H_{15}FO_2$: C, 66.65; H, 7.63. Found: C, 66.70; H, 7.65.

The enantiomeric ratio of **10** was determined by HPLC analysis after converted into corresponding naphthoate **26**. Naphthoate **26** was synthesized according to the procedure shown in Scheme S2. The crude mixture was purified by silica gel column chromatography (hexane : dichloromethane = 1 : 1) to give 87% yield of **26** as a diastereomeric mixture. All analytical data of **26** were obtained with a diastereomeric mixture.



exo-**26**

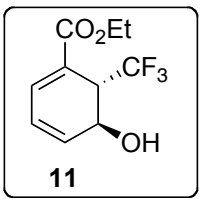
exo-**26**: $^1$H NMR (400 MHz, $CDCl_3$): δ 8.61 (s, 1H), 8.06 (dd, 1H, *J* = 8.5, 1.6 Hz), 7.99 -7.94 (m, 1H), 7.92-7.86 (m, 2H), 7.62-7.52 (m, 2H), 6.30 (dd, 1H, *J* = 5.4, 2.6 Hz), 6.11 (dd, 1H, 5.8, 3.2 Hz), 4.52-4.32 (m, 2H), 4.27-4.06 (m, 2H), 3.00 (brs, 1H), 2.84 (brs, 1H), 2.31-2.15 (m, 1H), 1.64-1.46 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 167.13, 138.26, 135.95, 134.44, 132.9, 131.47, 129.78, 128.69, 128.61, 128.17, 127. 82, 127.08, 125.57, 86.82 (d, *J* = 166.7 Hz), 68.68, 46.83, 44.78, 44.47, 44.05 (d, *J* = 4.0 Hz), 41.78 (d, *J* = 6.1 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$): δ –214.8 (td, *J* = 47.2, 10.6 Hz); The enantiomeric ratio was determined by HPLC (hexane : 2-propanol = 50 : 1, 1.0 mL/min) using a CHIRALCEL OJ-H column (0.46x 25 cm): major isomer 23.8 min and minor isomer 21.1 min.



endo-**26**

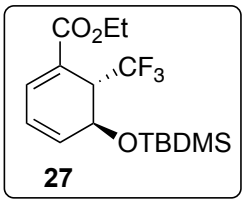
endo-**26**: $^1$H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 1H), 8.05 (dd, 1H, *J* = 8.6, 1.7 Hz), 7.99 -7.94 (m, 1H), 7.92-7.86 (m, 2H), 7.62-7.52 (m, 2H), 6.34-6.30 (m, 1H), 6.16 (dd, 1H, *J* = 5.6, 2.8 Hz), 4.70-4.32 (m, 2H), 4.27-4.06 (m, 2H), 3.00 (brs, 1H), 2.84 (brs, 1H), 2.31-2.15 (m, 1H), 1.64-1.46 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 167.03, 138.39, 135.91, 134.49, 132.88, 131.43, 129.78, 128.66, 128.60, 128.17, 127. 89, 127.08, 125.57, 86.89 (d, *J* = 169.0 Hz), 68.43, 46.72, 44.73, 44.35 (d, *J* = 3.8 Hz), 44.27, 42.15 (d, *J* = 5.7 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$): δ –214.6 (td, *J* = 47.1, 16.0 Hz); The enantiomeric ratio was determined by HPLC (hexane : 2-propanol = 50 : 1, 1.0 mL/min) using a CHIRALCEL OJ-H column (0.46x 25 cm): major isomer 26.2 min and minor isomer 18.8 min.

**Experimental procedure for Scheme 3 and characterization of new compounds.**



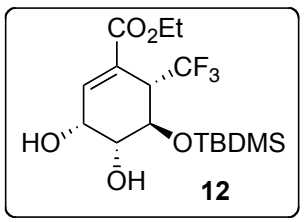
**11**

**11:** To a solution of **5b** (99% ee; 71 mg, 0.3 mmol) in THF (1.5 ml) was added LiHMDS (408 μl, 0.41 mmol) at -78 °C under argon atmosphere. The mixture was allowed to warm to 0 °C during 2 h. The mixture was then poured into $NH_4Cl$ aq at 0 °C. The aqueous layer was extracted with dichloromethane three times, and the combined organic extracts was dried over $Na_2SO_4$, and concentrated in *vacuo*. The crude mixture was purified by silica gel column chromatography (dichloromethane: ethyl acetate = 10 : 1) to give 76% yield of **11** as a colorless oil (99% ee): $^1$H NMR (400 MHz, $CDCl_3$) δ 7.36 (t, 1H, *J* = 3.6 Hz), 6.34-6.32 (m, 2H), 4.51 (brs, 1H), 4.35-4.21 (m, 2H), 3.92 (q, 1H, *J* = 9.6 Hz), 1.74 (d, 1H, *J* = 8.8 Hz), 1.33 (t, 3H, *J* = 7.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 166.15, 135.22, 131.51, 125.52 (q, *J* = 280.9 Hz), 124.69, 121.30, 61.50, 61.45 (q, *J* = 2.2 Hz) 44.75 (q, *J* = 25.9 Hz), 14.29; $^{19}$F NMR (376 MHz, $CDCl_3$): δ -70.3 (d, *J* = 10.5 Hz); $[\alpha]^{21}_D$ = +267.3 (*c* = 0.295, $CHCl_3$); FTIR (neat) $\upsilon_{max}$ 3425, 2986, 1713, 1651, 1586, 1369, 1321, 1253, 1164, 1126, 1075, 1022, 903, 876, 742 $cm^{-1}$; Anal. Calcd (%) for $C_{10}H_{11}F_3O_3$: C, 50.85; H, 4.69. Found: C, 50.80; H, 4.99.



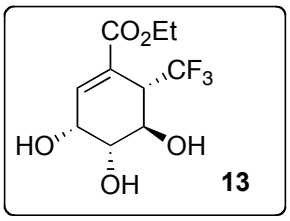
**27**

**27:** To a solution of 2,6-lutidine (47 µl, 0.41 mmol) in dichloromethane (200 µl) was added *t*-butyl dimethyl silyl trifluormethansulfonate (65 µl, 0.28 mmol) at 0 ˚C under argon atmosphere. After 30 min a solution of the **11** (43.7 mg, 0.185 mmol) in dichloromethane (800 µl) was added. The mixture was stirred for 1 h at 0 ˚C. The mixture was then poured into $NaHCO_3$ aq at 0 ˚C. The aqueous layer was extracted with dichloromethane three times, and the combined organic extracts was dried over $Na_2SO_4$, and concentrated in *vacuo*. The crude mixture was purified by silica gel column chromatography (hexane : dichloromethane = 1 : 1) to give 82% yield of **27** as a colorless oil (99% ee): $^1$H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, 1H, *J* = 6.0 Hz), 6.24 (dd, 1H, *J* = 9.2, 5.6 Hz), 6.15 (dd, 1H, *J* = 9.2, 5.2 Hz), 4.48 (d, 1H, *J* = 5.2 Hz), 4.30-4.24 (m, 2H), 3.76 (q, 1H, *J* = 10.0 Hz), 1.31 (t, 3H, *J* = 7.2 Hz), 0.87 (s, 9H), 0.13 (d, 6H, *J* = 11.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.10, 135.03, 131.73, 125.72 (q, *J* = 280.8 Hz), 123.70, 120.99 (d, *J* = 1.6 Hz), 61.94 (d, *J* = 2.3 Hz), 61.14, 45.20 (q, *J* = 25.6 Hz), 25.81, 18.18, 14.30, -4.32, -4.60; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -70.3 (d, *J* = 10.5 Hz); $[\alpha]^{19}_D$ = +200.3 (*c* = 0.425, $CHCl_3$); FTIR (neat) $\upsilon_{max}$ 2956, 2932,2859, 1715, 1651, 1588, 1472, 1405, 1362, 1317, 1278, 1245, 1166, 1126, 1105, 1058, 1005, 893, 837, 778, 728 cm$^{-1}$; Anal. Calcd (%) for $C_{16}H_{25}F_3O_3Si$: C, 54.84; H, 7.19. Found: C, 55.08; H, 6.97.



**12**

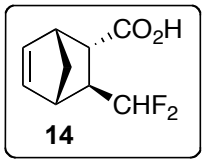
**12:** To a solution of **27** (53.3 mg, 0.15 mmol) in pyridine (1 ml) was added osmium tetroxide (39 mg, 0.15 mmol) at 0 ˚C under argon atmosphere. After 8 h at room temperature, aqueous sodium bisulphate (210mg of $Na_2S_2O$ in 3.6 ml of water) and pyridine (3 ml) were added successively. After *ca.* 20 min, the mixture, which turned orange, was extracted with dichloromethane three times, and the combined organic extracts was dried over $Na_2SO_4$, and concentrated in *vacuo*. The crude mixture was purified by silica gel column chromatography (dichloromethane : ethyl acetate = 10 : 1) to give 70% yield of **12** as a colorless oil (99% ee): $^1$H NMR (400 MHz, $CDCl_3$) δ 6.91 (d, 1H, *J* = 3.2 Hz), 4.48-4.46 (m, 2H), 4.29-4.22 (m, 2H), 3.85-3.82 (m, 1H), 3.50-3.43 (m, 1H), 2.73-2.52 (m, 2H), 1.31 (t, 1H, *J* = 7.2 Hz), 0.87 (s, 9H), 0.13 (d, 6H, *J* = 2.0 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.10, 140.26, 126.14 (d, *J* = 1.9 Hz), 125.24 (q, *J* = 280.4 Hz), 69.37, 68.92, 65.69, 61.54, 47.02 (q, *J* = 26.7 Hz), 25.75, 18.03, 14.13, -4.64, -5.04; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -62.7 (d, *J* = 10.2 Hz)**;** $[\alpha]^{19}_D$ = -9.3 (*c* = 0.500, $CHCl_3$); FTIR (neat) $\upsilon_{max}$ 3442, 2931, 2858, 1725, 1472, 1370, 1320, 1255, 1133, 1082, 1037, 940, 888, 836, 780 cm$^{-1}$; Anal. Calcd (%) for $C_{16}H_{27}F_3O_5Si$: C, 49.98; H, 7.08. Found: C, 49.66; H, 6.75.



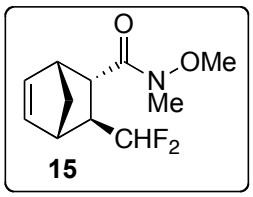
**13**

Ethyl 6-$CF_3$-sikimate (**13**)**:** To a solution of **12** (37.8 mg, 0.098 mmol) in THF (1 ml) was added tetrabutylammonium fluoride (196.6 µl, 0.196 mmol) at -78 ˚C under argon atmosphere. The mixture was stirred for 5.5 h at room temperature. The mixture was concentrated in *vacuo*. The crude mixture was purified by silica gel column chromatography (dichloromethane : ethyl acetate = 1 : 2) to give 78% yield of **13** as a colorless oil (99% ee): $^1$H NMR (400 MHz, $CDCl_3$) δ 6.88 (d, 1H, *J* = 5.6 Hz), 4.39 (s, 1H), 4.30-3.58 (m, 8H), 1.29 (t, 3H, *J* = 7.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.78, 137.72, 129.65, 125.98 (d, *J* = 280.8 Hz), 72.06, 66.18, 64.83, 61.99, 48.69 (q, *J* = 25.6 Hz), 13.98; $^{19}$F NMR (376 MHz, $CDCl_3$): δ -67.5 (d, *J* = 7.9 Hz); $[\alpha]^{19}_D$ = -86.3 (*c* = 1.335, $CHCl_3$); FTIR (neat) $\upsilon_{max}$ 3408, 2924, 1714, 1372, 1247, 1170, 1114, 1053, 938, 870, 767 cm$^{-1}$. Anal. Calcd (%) for $C_{10}H_{13}F_3O_5$: C, 44.45; H, 4.85. Found: C, 44.14; H, 5.33.

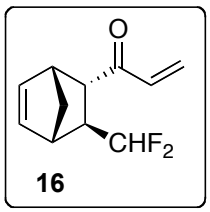
**Experimental procedure for Scheme 4 and characterization of new compounds**



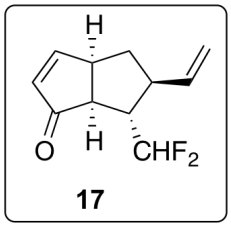

**14:** *endo*-**7** (99% ee; 95mg, 0.44 mmol) was refluxed with 10% aqueous sodium hydroxide (2 ml) for 2 h. After cooling, water (10 ml) was added, and the mixture was extracted with dichloromethane (2 ml). The aqueous fraction was acidified with 1.2 N HCl and extracted with dichloromethane (6 x 20 ml). The combined organic extracts were dried over $Na_2SO_4$, and concentrated to give **14** (70 mg, 85 %yield), which is pure enough to be used for next step without further purification: $^1$H NMR (400 MHz, $CDCl_3$) δ 6.33 (dd, 1H, *J* = 5.6, 3.6 Hz), 6.14 (dd, 1H, *J* = 6.0, 3.2 Hz), 5.84 (td, 1H, *J* = 56.4, 4.8 Hz), 3.30 (s, 1H) 3.00 (s, 1H), 2.95 (dd, 1H, *J* = 5.2, 3.6 Hz), 2.29-2.18 (m, 1H), 1.60 (d, 1H, *J* = 9.2 Hz), 1.51-1.49 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 179.09 138.36, 135.02, 117.87 (t, *J* = 240.7 Hz), 47.32, 46.78 (t, *J* = 20.6 Hz), 45.71, 45.11, 43.29 (t, *J* = 3.4 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$) δ -117.28 (ddd, *J* = 281.2, 57.2, 15.8 Hz), -119.55 (ddd, *J* = 281.6, 57.2, 16.2 Hz).




**15:** To a solution of carboxylic acid **14** (90 mg, 0.48 mmol) in 2 ml of dichloromethane, were added (benzotriazol-1-yloxy)–tris(dimethylamino)phosphonium hexafluorophosphate (211 mg, 0.48 mmol) and triethylamine (70 μl, 0.50 mmol). The resulting solution was stirred for 0.5 h, upon which time HNMe(OMe)•HCl (51 mg, 0.55 mmol) and triethylamine (70 μl, 0.50 mmol) were added. The mixture was stirred at room temperature for 24 h, then quenched with 1.2 N HCl. The aqueous layer was extracted with dichloromethane, and the combine organic layers were dried over $Na_2SO_4$, filtered, concentrated. The crude mixture was purified by silica gel column chromatography (hexane : ethyl acetate = 3 : 1) to give 83% yield of **15**: $^1$H NMR (400 MHz, $CDCl_3$) δ 6.33 (dd, 1H, *J* = 5.6, 3.2 Hz), 5.99 (dd, 1H, *J* = 6.0, 2.4 Hz), 5.84 (td, 1H, *J* = 57.2, 4.8 Hz), 3.74 (s, 3H) 3.24 (s, 1H), 3.20 (s, 1H), 3.18 (s, 3H), 2.97 (s, 1H), 2.49-2.39 (m, 1H), 1.64 (d, 1H, *J* = 8.8 Hz), 1.47 (d, 1H, *J* = 8.8 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 173.17 137.63, 118.32 (t, *J* = 240.4 Hz), 61.39, 48.01, 46.37 (t, *J* = 20.2 Hz), 45.97, 43.41 (t, *J* = 3.8 Hz), 41.76 (dd, *J* = 3.4, 2.3 Hz), 32.44; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -115.75 (ddd, *J* = 280.5, 56.0, 15.4 Hz), -119.62 (ddd, *J* = 280.1, 57.2, 16.9 Hz); $[\alpha]^{20}_D$ = +168.3 (*c* = 0.355, $CHCl_3$); FTIR (neat) $\upsilon_{max}$ 2974, 1661, 1385, 1334, 1180, 1137, 1112, 1048, 1008, 958, 862 cm$^{-1}$; Anal. Calcd (%) for $C_{11}H_{15}F_2NO_2$: C, 57.13; H, 6.54; N, 6.06. Found: C, 57.17; H, 6.34; N, 5.93.




**16:** Weinreb amide **15** (36mg, 0.16 mmol) was dissolved in 2ml of $Et_2O$, and the solution was cooled to -20 °C. Vinyl magnesium bromide (1.0 M in THF, 1.56 ml, 1.56 mmol) was added to this solution. The mixture was stirred at rt for 1.5 h, then quenched with aqueous $NH_4Cl$. The aqueous layer was extracted with $Et_2O$. The combined organic layers were dried over $Na_2SO_4$. The crude mixture was purified by silica gel column chromatography (hexane : ether = 8 : 1) to give 80% yield of **16**: $^1$H NMR (400 MHz, $CDCl_3$) δ 6.55 (dd, 1H, *J* = 17.6, 10.8 Hz), 6.33-6.28 (m, 2H), 5.91 (dd, 1H, *J* = 5.6, 2.8 Hz), 5.83 (td, 1H, *J* = 56.8, 4.8 Hz), 5.80 (dd, 1H, *J* = 11.6, 1.2 Hz) 3.29 (s, 1H), 3.25-3.23 (m, 1H), 2.99 (s, 1H), 2.53-2.42 (m, 1H), 1.69 (d, 1H, *J* = 8.8 Hz), 1.51 (d, 1H, *J* = 8.8 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 197.92, 138.07, 134.98, 133.73, 128.69, 118.16 (t, *J* = 240.7 Hz), 50.82, 47.61, 46.41, 44.71 (t, *J* = 20.2 Hz), 43.63 (d, *J* = 3.9 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$) δ -115.60 (ddd, *J* = 280.1, 57.2, 14.7 Hz), -119.39 (ddd, *J* = 282.1, 57.2, 16.9 Hz); $[\alpha]^{25}_D$ = +114.2 (*c* = 0.285, $CHCl_3$); FTIR (neat) $\upsilon_{max}$ 3050, 2982, 1697, 1679, 1614, 1403, 1333, 1258, 1213, 1135, 1106, 1051, 1006, 987, 858, 717 cm$^{-1}$; Anal. Calcd (%) for $C_{11}H_{12}F_2O$: C, 66.66; H, 6.10. Found: C, 66.70; H, 6.15.

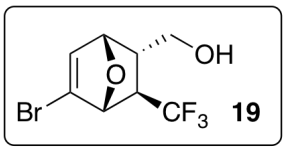


**17**

**17:** Compound **16** (27mg, 0.13 mmol) was dissolved in 13.5 ml dichloromethane. Ethylene was bubbled through this solution for ca. 5 min, followed by addition of Grubbs 1st generation catalyst (5.5 mg, 0.01mmol). The reaction flask was flushed with ethylene, and the reaction was allowed to stir for 20 h at room temperature under an ethylene balloon. The reaction was concentrated. The crude mixture was purified by silica gel column chromatography (hexane : ether= 3 : 1) to give 53% yield of **17**: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, 1H, *J* = 5.6, 2.8 Hz), 6.03 (dd, 1H, *J* = 5.6, 1.6 Hz), 5.97 (td, 1H, *J* = 56.4, 2.4 Hz), 5.68 (ddd, 1H, *J* = 17.6, 10.4, 8.0 Hz), 5.08-4.98 (m, 2H), 3.50-3.43 (m, 1H,), 2.95-2.87 (m, 2H), 2.29-2.17 (m, 2H), 1.36-1.25 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 210.32, 166.70, 139.18, 132.07, 116.51 (t, *J* = 240.7 Hz), 115.83, 50.07 (dd, *J* = 3.8, 2.7 Hz), 49.59 (t, *J* = 19.9 Hz), 47.46 (t, *J* = 4.6 Hz), 46.72, 14.32; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -123.39 (dd, *J* = 16.9, 13.5 Hz), -123.54 (dd, *J* = 16.9, 13.5 Hz); $[\alpha]^{22}_{D}$ = -70.5 (*c* = 0.310, $CHCl_3$); FTIR (neat) $\upsilon_{max}$ 3079, 2927, 1707, 1643, 1582, 1455, 1386, 1344, 1132, 1033, 906, 860, 803 $cm^{-1}$; Anal. Calcd (%) for $C_{11}H_{12}F_2O$: C, 66.66; H, 6.10. Found: C, 66.87; H, 6.26.

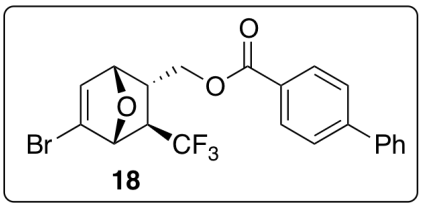
**Experimental procedure for Scheme 5 and X-ray crystallographic analysis.**

*Synthesis of **18***



**19**

Diels-Alder adduct **5c** (99% ee) was converted into 4-phenylbenzoate **18** according to the procedure shown in Scheme S2 (see page S8, 4-phenylbenzoyl chloride was used in acylation step instead of naphthoyl chloride). After $LiAlH_4$ reduction, the crude mixture was purified by silica gel column chromatography to give 88% yield of alcohol **19**: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.55 (d, 1H, *J* = 1.6 Hz), 5.09 (d, 1H, *J* = 3.6 Hz), 4.88 (s, 1H), 3.79 (dd, 1H, *J* = 10.8, 6.0 Hz), 3.30 (d, 1H, *J* = 10.0 Hz), 2.67-2.61 (m, 1H), 1.94 (qd, 1H, *J* = 9.2, 4.8 Hz), 1.63 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 134.60, 126.74 (q, *J* = 276.6 Hz), 125.53, 83.48 (d, *J* = 2.6 Hz), 81.93, 63.79, 45.96 (d, *J* = 27.8 Hz), 45.17; $^{19}$F NMR (376 MHz, $CDCl_3$): δ -68.30 (d, *J* = 9.0 Hz).



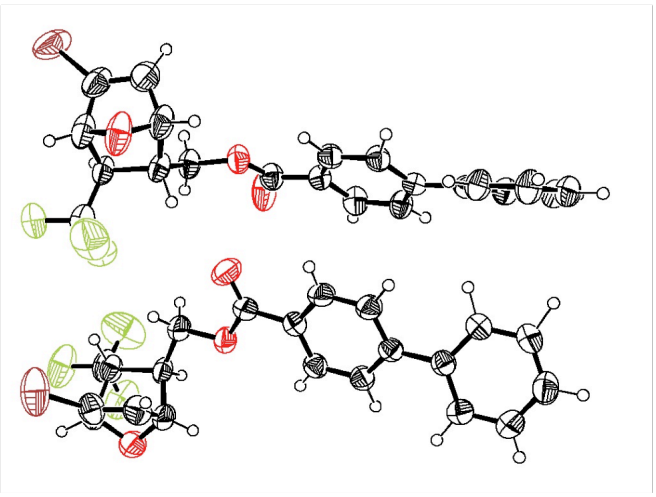
**18**

After acylation with 4-phenylbenzoyl chloride, the crude mixture was purified by silica gel column chromatography (hexane : dichloromethane = 1 : 1) to give 52% yield of **18** as a white crystal: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, 2H, *J* = 8.0 Hz), 7.68-7.38 (m, 7H), 6.58 (d, 1H, *J* = 2.0 Hz), 5.08 (d, 1H, *J* = 4.0 Hz), 4.93 (s, 1H), 4.27 (dd, 1H, *J* = 11.2, 6.4 Hz), 4.19 (dd, 1H, *J* = 11.6, 8.4 Hz), 2.19 (qd, 1H, *J* = 8.8, 5.2 Hz), 2.23-2.15 (m 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.14, 146.27, 139.90, 134.42, 130.31, 129.09, 128.42, 128.14, 127.40, 127.31, 126.59 (q, *J* = 276.6 Hz), 126.18, 83.70 (d, *J* = 2.3 Hz), 81.71, 64.77, 46.72 (q, *J* = 28.2 Hz), 42.39; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -68.29 (d, *J* = 8.3 Hz).

*X-ray crystallographic analysis of **18***

Single crystals were obtained by slow evaporation of the solution dissolving the compound in diethyl ether and methanol. Diffraction data were collected on a Rigaku Mercury CCD diffractometer with rotating anode and graphite-monochromated Mo *Kα* radiation (λ=0.71069 A). All experimental procedures were carried out at the room temperature. Data reduction, cell refinement and semi-empirical absorption correction were performed using the Rigaku CrystalClear software package up to a maximum θ angle of 29.13° (0.73 Å resolution) using the 3D profile fitting method. The crystal system and space group were determined using Yadokari-SG 2009 (Wakita and Akine). The structure was solved using Yadokari-XG 2009 (Wakita and Nemoto) by the direct method using SIR2004 (Burla, Caliandro et al., 2005) and refined by the full-matrix least squares procedure on $F^2$ using SHELXL (Sheldrick, 2008). All non-H atoms were refined with anisotropic displacement parameters. All hydrogen atoms were found in difference-Fourier maps and refined with isotropic displacement parameters.

**Figure S5. ORTEP Drawing of 18**



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